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(71) Applicant
Imperial Chemical Industries Plc

(Incorporated in the United Kingdom)

Imperial Chemical House, Millbank, London, SW1P 3JF, United Kingdom

(72) Inventor
Neil Tindale

(74) Agent and/or Address for Service
John George Graham
Imperial Chemical Industries Plc, Legal Dept: Patents, PO Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire, AL7 1HD, United Kingdom

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(54) **Polyesters**

(57) Polyester compositions (blends or copolymers) containing between 0.001 mole % and 5 mole %, preferably between 0.01 mole % and 4.5 mole %, of napthalene dicarboxylate, preferably 2, 6-naphthalene dicarboxylate, residues to increase the wavelength range over which the composition absorbs UV radiation.

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Polyesters

This invention relates to polyesters.

The use of polyester, particularly polyethylene terephthalate (PET), for example in the form of films, bottles and other containers, as a packaging material is well known. However, many goods, for example foodstuffs, fruits juices, soft drinks and cosmetic and pharmaceutical preparations, are deleteriously affected by ultraviolet radiation (UV) substantially in the wavelength range 250 nm to 360 nm. Thus, such goods, when packaged in clear, colourless PET material (which absorbs UV upto 320 nm), can deteriorate relatively rapidly and, consequently, only have a limited shelf life. To some extent the problem can be alleviated by adding fillers and/or dyes to PET which absorb UV in the region 320 nm to 360 nm.

The Applicants have found that polyester compositions which include surprisingly small amounts of naphthalene dicarboxylate residues absorb significant amounts of UV, typically 90% of the incident UV, in the region 320 nm to 360 nm. Such compositions are also clear and colourless as made.

Thus, according to the present invention, a thermoplastic polyester composition comprises a polyester which contains at least 50 mole %, preferably at least 70 mole %, of ethylene terephthalate residues and which contains, or comprises a blend with a second polyester containing, between 0.001 mole % and 5 mole % of naphthalene dicarboxylate residues.

Preferably, the first polyester comprises either a copolymer containing only ethylene terephthalate and ethylene naphthalate residues or, when blended with the second polyester, a homopolymer of ethylene terephthalate residues.

When the composition comprises a blend, preferably the second polyester is a homopolymer of ethylene naphthalate residues.

Alternatively, the first polyester may also contain residues derived from ethylene isophthalate, ethoxyethylene terephthalate, ethoxyethylene isophthalate or ethoxyethylene naphthalate.

Similarly, the second polyester may contain residues derived from ethylene terephthalate, ethylene isophthalate, ethoxyethylene terephthalate, ethoxyethylene isophthalate or ethoxyethylene naphthalate.

The composition can also contain other additives and/or lubricants such as catalysts, stabilisers, processing aids, antioxidants, fillers, plasticisers and nucleating agents as is well known in the art.

Preferably, the amount of naphthalene dicarboxylate residues present is in the range 0.01 mole % to 4.5 mole %.

Preferably, the amount of naphthalene dicarboxylate residues present in the composition is selected such that, when the composition is formed into a packaging material, eg a film, bottle or other like container, the material will absorb at least 50%, and preferably at least 90%, of incident ultraviolet radiation in the region upto 360 nm falling thereon.

Preferably, the naphthalene dicarboxylate residues are derived from 2,6-naphthalene dicarboxylic acid or a diester thereof.

Typically, polyesters such as PET are made by firstly reacting a glycol with a dicarboxylic acid or dimethyl ester thereof to produce a pre-polymer compound which is then polycondensed to produce the polyester. If required, the molecular weight of the polyester is then increased further by solid-phase polymerisation.

When the composition comprises a polyester containing naphthalene dicarboxylate residues, the naphthalene dicarboxylate residues can be readily incorporated into the polymer by adding the required mole % of naphthalene dicarboxylic acid, or dimethyl ester thereof, to the glycol and diacid or diester reaction mixture or of naphthalene dicarboxylic acid to the pre-polymer compound for incorporation into the polymer during the polycondensation reaction.

The second polyester can be made in a similar manner.

The invention includes packaging material made from a thermoplastic polyester composition according to the invention.

The invention will now be illustrated by reference to the following Examples.

Example 1

From the proportionality implied by the Beer-Lambert law, the Applicants have derived the following empirical formula I for determining the amount "x" mole % of naphthalene dicarboxylate residues required in the thermoplastic polyester composition to absorb at least 90% of the incident UV radiation up to 360 nm in packaging material of thickness "y" mm:-

$$x = \frac{0.0857}{y} \qquad \text{I}$$

Thus, for example, for a bottle (eg for soft drinks) having a wall thickness of 0.3 mm, x = 0.29 mole %; for a film (eg for wrapping food stuffs having a thickness of 0.02 mm, x = 4.38 mole %; and for a container (eg for cosmetic preparations) having a wall thickness of 10 mm, x = 0.009 mole %.

Example 2

Stage 1: Dimethyl terephthalate (7.07 Kg, 36.5 mole), ethylene glycol (5.2 Kg, 83.8 mole) and dimethyl - 2, 6-naphthalene dicarboxylate (26.8g, 0.11 mol) were stirred together and heated from 150 to 250°C over a period of 2 hours at atmospheric pressure in the presence of a catalyst (manganese acetate). An ester interchange reaction occurred with the evolution of methanol to give a reaction mixture of di (hydroxyethyl) terephthalate and di (hydroxyethyl) naphthalate.

Stage 2: The reaction mixture was then heated further to 290°C and a vacuum of 0.4 mm Hg was applied. A catalyst (antimony trioxide) and a stabiliser (phosphoric acid) were added. Under those conditions, the reaction mixture underwent a polycondensation reaction with the evolution of ethylene glycol to form a polyester containing 0.3 mole % of naphthalene dicarboxylate residues. The polymer had a number average molecular weight in the range 10,000 to 25,000.

Example 3

Stage 1: Terephthalic acid (6.05 kg, 36.45 mole), ethylene glycol (2.7 Kg, 43.7 mole) and 2,6 - naphthalene dicarboxylic acid (23.6g, 0.11 mole) were stirred together and heated to 250°C under a nitrogen pressure of 56 psig. Water was evolved during the resultant esterification reaction. The reaction mixture now consisted of low molecular weight polyester pre-polymer.

Stage 2: The reaction mixture was then further reacted under the same conditions as described for Example 2, Stage 2. The resultant polyester contained 0.3 mole % of naphthalylene dicarboxylate residues and had a number average molecular weight of between 10,000 and 25,000.

Example 4

Stage 1: Polyester pre-polymer was prepared by the procedure described in Example 3, Stage 1 except that no 2,6 - naphthalene dicarboxylic acid was used.

Stage 2: 2,6 - naphthalyne dicarboxylic acid (23.6 g, 0.11 mole) was then added to the molten pre-polymer and the mixture was stirred for 5 minutes. The reaction was then further reacted under the same conditions as described for Example 2, Stage 2. The resultant polyester contained 0.3 mole % of naphthalene dicarboxylate residues and had a number average molecular weight of between 10,000 and 25,000.

Example 5

Powdered polymers from Examples 2 to 4 were moulded into 0.10 mm thick transparent films in a film press at about 300°C. The UV absorption spectra were determined. The spectra showed the least intense UV absorption by the film in the wavelength range of 320 nm to 360 nm occurred at about 330 nm. The absorption at this point was 0.35 absorbance units.

Example 6

Polymer from Example 4 was formed into typical carbonated soft drink bottles having a wall thickness of 0.3 mm by injection moulding a bottle preform and stretch-blow moulding the preform. The UV absorption spectrum of one such bottle was determined. From the spectrum, the absorption coefficient was at least 1.0 absorbance unit at all wavelengths shorter than 360 nm indicating that the polymer was absorbing at least 90% of the incident UV radiation.

Example 7

Two polymer blends were prepared from polyethyleneterephthalate and polyethylene naphthalate and a copolymer of 50% ethylene terephthalate and 50% ethylenenaphthalate residues, respectively, by dry mixing chips of the respective polymers to achieve a substantially homogenous mixture. The two homopolymer blend (blend 1) contained 2.0 mole % of 2,6 - naphthalene dicarboxylate residues and the homopolymer/copolymer blend (blend 2) contained 0.50 mole % of such residues.

Example 8

Blends 1 and 2 from Example 6 were moulded in a film press at about 300°C into 0.10 mm transparent films and the UV spectra of the films determined similarly to Example 5. The spectra showed the film of blend 1 had an absorbance of 2.30 absorbance units and the film of blend 2 had an absorbance of 0.58 absorbance units at the wavelength of least absorbance, namely 330 nm.

Thus, in accordance with the formula I in Example 1, blends 1 and 2 can be used for material having a thickness as low as 0.04 mm and 0.15 mm, respectively.

Example 9

Bottles having a wall thickness of 0.3 mm were moulded from PET and from a polymer made in accordance with Example 3. The bottles were filled with a 7.27×10^{-3}% by weight aqueous solution of quinine. The solution - containing bottles were then exposed to natural light for one month by being placed next to a glass window. During that period, small samples were periodically removed from each bottle and the absorbance of the respective samples at 360 nm determined to check the level of yellowness of the samples, the level of yellowness being an indication of the onset of degradation of the quinine. These tests indicated the intensity of yellowness of the solution in the PET bottle increased approximately at five times the rate at which the intensity of yellowness of the solution in the bottle made from polymer according to the invention.

CLAIMS

1. A thermoplastic polyester composition comprising a polyester which contains at least 50 mole %, preferably at least 70 mole %, of ethylene terephthalate residues and which contains, or comprises a blend with a second polyester containing, between 0.001 mole % and 5 mole % of naphthalene dicarboxylate residues.

2. A composition according to claim 1, in which the first polyester comprises either a copolymer containing only ethylene terephthalate and ethylene naphthalate residues or, when blended with the second polyester, a homopolymer of ethylene terephthalate residues.

3. A composition according to claim 1 or claim 2, in which, when the composition comprises a blend, the second polyester is a homopolymer of ethylene naphthalate residues.

4. A composition according to claim 1, in which the first polyester contains residues derived from ethylene terephthalate, ethoxyethylene terephthalate, ethoxyethylene isophthalate or ethoxyethylene naphthalate.

5. A composition according to claim 1 or claim 2, in which the second polyester contains residues derived from ethylene terephthalate, ethylene isophthalate, ethoxyethylene terephthalate, ethoxyethylene isophthalate or ethoxyethylene naphthalate.

6. A composition according to any one of the preceding claims, in which the amount of naphthalene dicarboxylate residues present is in the range 0.01 mole % to 4.5 mole %.

7. A composition according to any one of the preceding claims, in which the amount of naphthalene dicarboxylate residues present in the composition is selected such that, when the composition is formed into a packaging material, the material will absorb at least 50%, and preferably at least 90%, of incident ultraviolet radiation in the region up to 360 nm falling thereon.

8. A composition according to any one of the preceding claims, in which the naphthalene dicarboxylate residues are derived from 2,6-naphthalene dicarboxylic acid or a diester thereof.

9. A packaging material made from a thermoplastic polyester composition according to any one of the prec ding claims.

10. A composition according to claim 1 substantially as hereinbefore described with reference to the accompanying Examples.

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